

# PATENT SPECIFICATION

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## (54) METHOD OF SEPARATING COAL FROM ITS ACCOMPANYING GANGUE

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The coal mining industry has recently come under pressure from the environmentally conscious community to remove the large quantities of tailings which have accumulated over the years. The amounts of tailings are projected to increase more rapidly in the future because coal is expected to be mined at an increased rate.

The coal mining industry has used and is today using dense media separation techniques as well as froth-flotation, in some instances in series, to reduce the iron pyrites which contribute to the ash in coal as well as sulfur gases on combustion of the coal containing the pyrites. In addition, these steps also upgrade the coal by reducing the clays and shale associated with the coal, both of which also contribute the major residue known as ash on combustion of the coal. These treatments, known in the art as concentrating (benefaction), because the clays and pyrites contents are reduced, produce a parting liquid, usually water, containing large volumes of coal fines and clay fines, i.e., usually less than about 28 mesh (Tyler Sieve Series), particularly in respect to treatment of coal which has been crushed and sized for use in stoker-fed boilers or other heat-generating apparatus known as "steam coal" as well as metallurgical coal (i.e., coking coal) for use in making steels and casting irons. The slurries of fines resulting from these treatments are pumped to tailings piles or ponds where the water runs off and in many instances is collected and reused. The tailings presently being discharged are in the form of a water slurry, the solids being mainly clays and coal with small amounts of other impurities, i.e., pyrite, quartz, etc., of which from 10 percent to 60 percent is coal. It is estimated that several million tons of solids are discarded onto the landscape each year. The coal content, if recoverable, could be a significant addition to our short energy supply.

Therefore, it is desirable to provide a process for separating the coal from the other solids (hereinafter referred to as "gangue") in the mine tailings slurries.

The present invention is a method for separating coal from its accompanying gangue comprising

treating finely divided gangue-coal with water and a water-immiscible organic liquid, said liquid having a specific gravity sufficiently greater than water to permit, after treatment has taken place, phase separation of the water and organic liquid, and

removing the gangue with the water and the coal with the organic liquid as a slurry.

The water may be that used to transport the coal in a coal preparation process or may be added or drained to adjust to the appropriate water to solids content and the organic liquid added.

The phenomenon of separation of the coal and the gangue is similar to washing the gangue away from the coal as compared to the sink-float technique or froth-flotation which latter processes require the organic liquid to have a density greater than the coal and less than the gangue. In the instant aspect of the present invention the coal, which has a density less than the gangue, remains with the organic liquid and the gangue, which has a density greater than the coal, disperses in the water phase. This selective extraction is a result of wettability differences of coal and gangue with the organic liquid and water and is not

related to differences in specific gravity differences of the respective solid materials. This phenomenon permits a dry (with respect to water) coal to be obtained and gangue suspended in water and which is capable of precipitation from the water by high molecular weight polymeric flocculating agents or cationic surfactive agents.

5 It may be advantageous to add a surface-active agent to the water and organic liquid mixture. In some instances, such as in batch operations, the surfactants may be added to the point of producing an emulsion. However, in continuous operations it is preferred to use only a small amount of surface-active agent, i.e., from 0.01 to 0.05 grams per 320 milliliters of water and organic liquid when, for example, an octylphenoxypolyethoxyethanol is used. 10 It is to be clearly understood that other surface-active agents will be required in greater or lesser quantities, depending on the strength of the surface-active agent in the formulation employed, as well as the class of surface-active agents and its structure. Among the surfactants found useful, i.e., compatible with the present invention liquid systems, are the nonionics such as N,N-dimethylecates, modified oxyethylated straight chain alcohols, 15 propylene oxide-ethylene diamine-ethylene oxide condensates having an average molecular weight of about 700, polyethoxy ethers, condensates of ethylene oxide and propylene glycol, polyethylene monolaurates, an octylphenoxypolyethoxyethanol, a nonylphenol ethylene oxide adduct containing about 100 moles of ethylene oxide, and alkali metal petroleum sulfonates, or the anionic surfactants such as the alkylbenzene sulfonates, tetra- 20raisopropyl benzene sulfonate and dodecylbenzene sulfonate. When these surface-active agents are added in larger quantities, i.e., from 0.15 or more grams of, for example octylphenoxypolyethoxyethanol per 320 ml of water and organic liquid, an emulsion usually results. The exact amount of surface-active agent which may be added varies with the specific surface-active agent and may be readily ascertained by adding the surface-active 25 agent to proportionate amounts of the particular water-organic liquid mixture and stirring the resulting mixture to determine whether an emulsion occurs. While the above discussion has been directed to the test for emulsion as previously stated, it is preferred to use an amount of surface-active agent less than that which forms the emulsion. From 0.01 to 0.05 grams per 320 ml of the mixture seems to be adequate and, in those instances tested using 30 the above-enumerated surface-active agents, did not form emulsions under the conditions of the stirring and separation in accordance with the present invention.

Substantially any organic liquid immiscible with water and having a density greater than water such that gravity separation of the solvent and water can occur is suitable. It is to be understood that in this aspect of the present invention the solvent can be of any density 35 greater than water, and where the solvent can be phase-separated from water. However, the preferred organic liquids, from a safety and ecological standpoint, as well as for economic reasons, are the halogenated  $C_1$  to  $C_4$  hydrocarbons having 2 to 6 halogen atoms and a specific gravity of at least 1.30. The most preferred of this class of organic liquids are perchloroethylene (tetrachloroethylene), methylene chloride and 1,1,1-trichloroethane, 40 since these have specific gravities of about 1.6, 1.322 and 1.33 respectively, are substantially immiscible with water, can be recovered by water condenser systems for reuse, do not react with the coal or clay, are not flammable by Tag Open Cup Flammability Test and have low heats of vaporization so that they can be freed from the coal readily and from the water by simple water separators. Additionally, these solvents are compatible with other liquids 45 used in the coal industry, i.e., those used for froth-flotation and pyrite removals.

The amounts of water and organic liquid which have been found advantageous for rapid non-emulsion type continuous operations above-described are in the range of 4 to 50 parts by weight of water per part by weight of solids and 1 to 70 parts by weight of organic liquid per part by weight of solids. The preferred ranges are 6 to 20 parts water per part of solids and 1 to 5 parts by weight of organic liquid per part by weight of solids. 50

A single contact of the gangue-coal with a high ratio of water and organic liquid to solids mixture, under agitation, will upon settling reduce the gangue content of the coal considerably, that is, as much as 40 percent to 60 percent of the gangue associated with the coal is released and removed. However, it may be advantageous to employ the ratios mentioned 55 above and to conduct several such mixings and settlings. It has been observed that the gangue content of the coal is substantially reduced with each subsequent treatment.

An alternative method for separating the coal-organic phase from the gangue-water phase is centrifuging as, for example, in a cyclone separator, i.e., a hydrocyclone. Although a conventional centrifuge may be used, the energy expended far exceeds that which is 60 required to operate a cyclone. The advantage of using one or more cyclones is the ease of separation, standard pumps known in the coal processing industry can be used, the power or energy requirements are reasonable, and adjustments in flow can be made readily to alter the distribution of the coal-organic stream to very low gangue content or moderate gangue content. 65

In another aspect of the present invention a coarse coal can be freed of gangue by treating 65

the coal with a mixture of water and an organic liquid, which in this aspect of the invention has a density equal to or greater than the density of coal. The water is present in an amount of 0.1 to 4 parts by weight per part by weight of solids and the organic liquid is present in at least 1 part by weight per part by weight of solids and the coal is separated from the gangue using either a hydrocyclone or settling-skimmers or a combination, i.e., skimming the underflow after settling. Using this treatment a low sulfur, low ash coal can be recovered.

Figure 1 is a block flow diagram illustrating the high-water, high-solvent to solids ratio aspect of the present invention.

Figure 2 is a more detailed, modified schematic diagram of a flow chart related to Example 5.

Figure 3 is a more detailed, modified schematic diagram of a flow chart related to Example 6.

Figure 4 is a more detailed, modified schematic diagram of a flow chart related to Example 7.

Figure 5 is a more detailed, modified schematic diagram of a flow chart related to Example 8.

Example 1.

A mine tailings aqueous slurry obtained from a thickener following a froth-flotation treatment was added to a perchloroethylene-water mixture adjusted to provide, based on the solids weight, 10 parts of water and 5 parts of perchloroethylene each per part of tailings. The resulting mixture was agitated vigorously for 15-30 seconds. Upon stopping the agitation the coal and perchloroethylene settled rapidly, in 15-30 seconds, to the bottom of the container. Upon decantation of the water layer which contains most of the clay, two additional aliquots of water (about 10 parts) were shaken with and decanted from the perchloroethylene. The coal was recovered by filtration from the perchloroethylene. Analysis showed that over 45 percent of the original tailing was recovered as coal product. The ash content of this sample was 8.37 percent.

Other runs were made as above using various surfactants and the results tabulated below.

	<i>Surfactant</i>	<i>Ash %</i>	
30	1. None	8.37	30
	2. Propylene oxide-ethylenediamine-ethylene oxide condensate, mol. wt. 702, HLB 7.0	8.36	
35	3. Modified oxyethylated straight chain alcohol, HLB 7.0	9.17	35
	4. Condensate of ethylene oxide and propylene glycol, HLB 27.5	10.9	
40	5. Nonyl phenol-ethylene oxide adduct containing about 100 moles ethylene oxide, HLB 19.0	13.22	40
	6. N,N'-dimethyl oleamide, HLB 7.0	9.42	
	7. Nonylphenoxy poly(ethyleneoxy) ethanol	9.19	
45	8. Isopropylamine dodecylbenzene Sulfonate	12.1	45

All of the coal cuts filtered easily

Example 2.

In another example mine tailings were mixed with various ratios of water and perchloroethylene, by agitating 15 grams of the tailings in the selected water-perchloroethylene system, allowing the two liquids to settle and measuring and analyzing the coal for ash content. The solvent phase was washed with a second aliquot of water in all but one run. The results of the several runs are set forth in the table below.

	Water, gm	Perchloro- ethylene, gm	Ratio Water solids	per solids	Cycles	Ash % in Coal	
5	75 <sup>1</sup>	40 gm	5	2.66	2	22.6	5
	150	40 gm	10	2.66	1	21.6	
	100 <sup>1</sup>	40 gm	6.66	2.66	2	15.6	
	150 <sup>1</sup>	40 gm	10	2.66	2	16.39	
	150 <sup>1,2</sup>	40 gm	10	2.66	2	14.94	
10	150	72 gm	10	4.8	2	12.75	10

<sup>1</sup>Each wash.

<sup>2</sup>Laboratory blender used to mix.

- 15 A representative flow diagram of the present process is set forth in the drawings, Figure 1. A feed, an aqueous slurry of coal and clay, is admixed with additional water to bring the water to solids content in the range of 6 to 50 parts of water per part of solid and with an organic solvent to bring the solvent to solids content, in the range of 2 to 70 parts of solvent per part of solid. The mixing should be of sufficient agitation to insure that the water and solvent are thoroughly mixed and that the coal and clay are distributed to contact the water and solvent to insure that each particle of solid has a change to selectively be wet by the solvent or water. The well-mixed slurry is then forwarded to a separator, e.g., a cyclone separator, wherein the water and solvent separate by specific gravity differences and their mutual immiscibility. The coal will, for the greater part, stay with the solvent, and the clay with the water. A layer of oil-solvent and some water resulting from extraction of the oil in the coal will form on the top of the water layer, or in the case of the cyclone will come over with the water or can be recovered as separate stream. Decantation, or separation as in a cyclone, of the layers one from the other results in a clay-water fraction, which, after skimming to remove the oil-solvent-water scum, can be sent to a settling pond for dewatering. The coal-solvent fraction is readily filtered. The solvent is sent to a water separator, then to storage for return to the process. The coal may be freed of residual solvent in a dryer and the solvent vapors condensed and sent to the water separator. The solvent may extract oil from the coal and, if so, is freed of oil on a continuous or semi-continuous basis by sending the solvent to a still, condensing it and returning it to storage.
- 35 The foregoing description, with particular reference to the use of a cyclone separator, is a presently conceived, preferred scheme for utilizing the present invention in actual practice.

Example 3.

- 40 In another example, 10 grams of dried solids from a mine tailings containing about 50 percent ash and 50 percent coal was mixed with perchloroethylene and water containing 0.01 gram of detergent (HLB 18 prepared from ATLAB Test Kit Model HLB 1). The agitated mixture was permitted to separate into two phases, the water phase was decanted, the perchloroethylene phase filtered, and the filter cake dried and analyzed. The result of two such operations are set forth below:

	Solids gm	H <sub>2</sub> O gm	Perchloro- ethylene gm	Percent Coal/Ash Content	
45	10	300	ca 320	23	45
	10	400	ca 160	25	

- 50 Example 4.

In an additional run several organic liquids were used in the following manner.

- 55 In each of a series of experiments 100 ml of a 10 percent slurry of mine tailings (50.6 percent ash, 49.4 percent coal, dry weight) was mixed with 50 cc. of a solvent. The phases were permitted to separate, the water phase decanted and the solvent phase remixed with about 200 ml. water shaken, decanted twice. The resulting solvent phase was filtered and the cake dried. Analysis for ash content was made. The results are set forth in the following table.

	Solvent	% Ash Content	
60	1,1,1-Trichloroethane	12.42	60
	Methylene Chloride	7.56	
	Bromoform	8.0	
	Freon 113	9.95	
65	Carbon Tetrachloride	7.12	65

#### Example 5.

Figure 2 illustrates in schematic manner a flow diagram of a coal processing operation in which a residue (tailings or gangue) from a hydrocyclone separation technique for wet concentration of fine coal is employed. The run of the mine (ROM) coal having a sulfur content of 1.74 percent and a 19.6 percent ash content is crushed and screened. The coal then has a 1.7 percent sulfur content and 17.23 percent ash content. This 20 m x 0 coal is slurried with water, in this instance to make a 10 percent solids in water slurry. The slurry is decanted and the decantate (about 45 percent of the coal) is pumped to a three inch (7.62 cm.) hydrocyclone at a rate of 200 U.S. gallons (755.1.) per hour and the cyclone adjusted to take about 44 percent of the solids over as about a 5 percent slurry in water (the gangue, tailings or residue) and about 56 percent as underflow or bottoms as a saleable coal, i.e., having a reduced ash content, i.e., 16.17 percent ash. The sulfur content of this particular coal was 2.29 percent.

The overhead was mixed with perchloroethylene, to provide about a 4 to 1 perchloroethylene ratio by weight per part of solid, and fed to a hydrocyclone, at a ratio of 200 U.S. gallons per hour (755.1.) The hydrocyclone was adjusted to take 52 percent solids overhead (clay and water) and a 48 percent solids underflow (bottoms), coal and perchloroethylene, the coal having 1.53 percent sulfur and 5.6 percent ash content.

#### Example 6

Treatment of the coal which remained from the slurry decantation, about 55 percent, is illustrated in Figure 3 and demonstrates the alternative procedure within the invention. The coal was drained and found to contain 1.59 percent sulfur and a 10.47 percent ash content. This coal was slurried with perchloroethylene in a ratio of about 4 parts perchloroethylene per part solids and hydrocycloned. The overhead, about 64 percent of the solids, had a sulfur content of 1.41 percent and an ash content of 6.76 percent. The underflow from this hydrocyclone, about 36 percent of the solids feed, had a sulfur content of about 2.07 percent and an ash content of about 17.72 percent.

This example illustrates the versatility of the present invention to recover valuable coal from coal preparation tailings (gangue or residue), as well as a low sulfur, low ash coal from conventional saleable coal as now prepared by the industry.

#### Example 7

In a still further example, as illustrated in Figure 4, the ROM coal crushed to 8 m x 0 was screened to provide a 20 m x 0 screen and an 8 m x 28 m size. The 20 m x 0 size was treated with water in a hydrocyclone to yield a 55 to 60 percent overhead residue (gangue or tailings) and a 40-45 percent underflow coal having 2.97 percent sulfur and 34.54 percent ash. The overhead flow was treated as in the above example by mixing with about 4 parts of perchloroethylene per part of solids and hydrocycloning to a 55 percent overhead (clay and water) and an underflow (bottoms) of coal having 1.47 percent sulfur and 4.37 percent ash. The underflow from the first hydrocyclone was drained and mixed with about 4 parts of perchloroethylene per part of solids and hydrocycloned. The overhead contained 93.8 percent of the solids as a coal having 1.71 percent sulfur and 9.55 percent ash and a bottoms, 6.2 percent, having 3.52 percent sulfur and 38.6 percent ash.

#### Example 8.

In a still further example of the applicability of the present invention, as illustrated in Figure 5 a tailings obtained from a mine preparing coal using hydrocyclones was mixed with perchloroethylene and water to provide a ratio of water to solids and perchloroethylene to solids at 4 to 1 and 1.3 to 1, respectively. This slurry was treated in a first hydrocyclone and the clay-water fraction was drawn off at the top, while the coal-perchloroethylene fraction was taken off at the bottom and was a saleable grade of coal. The clay-water fraction was treated with additional perchloroethylene and passed into a second hydrocyclone adjusted to flow out at the top at about a 55 percent solids content. This outflow was a 10.6 percent solids (clays) slurry in water. The bottoms from this cyclone, 45 percent of the solids was coal in perchloroethylene which was fed to a third hydrocyclone to provide a top outflow of 69 percent of solids (coal, 3.44 percent sulfur, 6.38 percent ash) and a bottoms, 31 percent, which was allowed to settle, then skimmed. Ninety-three percent of the bottoms solids was skimmed off. This skim contained 4.11 percent sulfur and 7.07 percent ash. The sink contained 18.15 percent sulfur and 40.5 percent ash. This example illustrates the value of the treatment of the present invention for removing sulfur in addition to removing ash. The order of the various steps has been demonstrated to be flexible with desirable results for each order.

#### WHAT WE CLAIM IS:-

1. A method for separating coal from its accompanying gangue which comprises (a) treating finely divided gangue-coal with water and a water-immiscible organic liquid, said liquid having a specific gravity sufficiently greater than water to permit, after treatment has taken place, phase separation of the water and the organic liquid, and

- (b) removing the gangue with the water, and the coal with the organic liquid as a slurry.
2. A method as claimed in claim 1, wherein the finely divided gangue-coal is treated with an organic liquid-water mixture.
3. A method as claimed in claim 2 in which the organic liquid-water mixture contains a surface-active agent. 5
4. A method as claimed in claim 3 in which the surface-active agent is present in an amount sufficient to form an emulsion with at least a part of the water and organic liquid.
5. A method as claimed in claim 3 in which the surface-active agent is present in an amount less than that which will emulsify any part of the water and organic liquid.
- 10 6. A method as claimed in any one of the preceding claims in which the organic liquid is a halogenated hydrocarbon having from 1 to 4 carbon atoms, from 2 to 6 halogen atoms, and a specific gravity of at least 1.30. 10
7. A method as claimed in any one of the preceding claims in which water is used in an amount of 4 to 50 parts by weight per part by weight of solids.
- 15 8. A method as claimed in claim 7 in which the amount of water is 6 to 20 parts by weight per part by weight of solids. 15
9. A method as claimed in any one of the preceding claims in which the organic liquid is used in an amount of 1 to 70 parts by weight per part by weight of solids.
10. A method as claimed in claim 9 in which the amount of the organic liquid is 1 to 5 parts by weight per part by weight of solids. 20
11. A method as claimed in any one of claims 1 to 6 in which water is used in an amount of 0.1 to 4 parts by weight per part by weight of solids. 20
12. A method as claimed in any one of claims 1 to 6 and 11 in which the organic liquid is used in an amount of at least 1 part by weight per part by weight of solids.
- 25 13. A method for separating coal substantially as hereinbefore described in any one of Examples 1 to 4. 25
14. A method for separating coal substantially as hereinbefore described with reference to and as illustrated in Figure 1 of the accompanying drawings.
15. A method for separating coal substantially as hereinbefore described in any one of Examples 5 to 8. 30
16. A method for separating coal substantially as hereinbefore described with reference to and as illustrated in any one of Figures 2 to 5 of the accompanying drawings.
17. Coal which has been separated by a method as claimed in any one of the preceding claims. 35

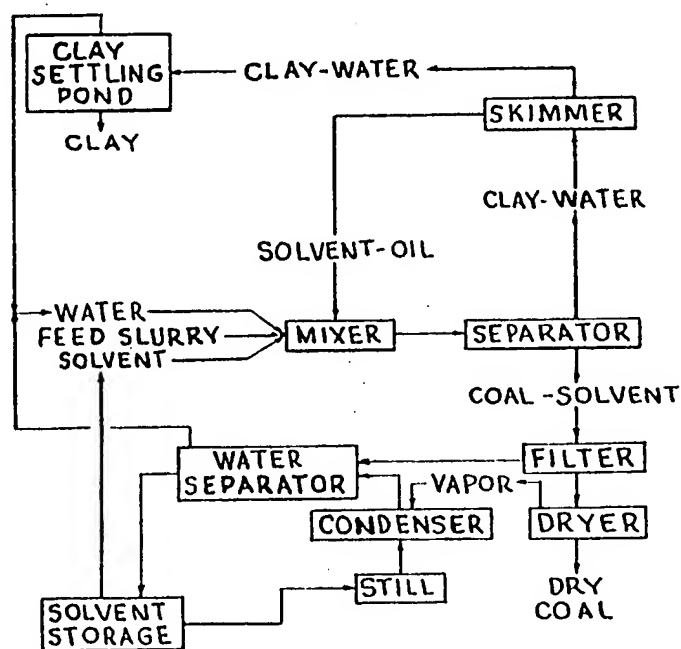
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*Fig. 1*

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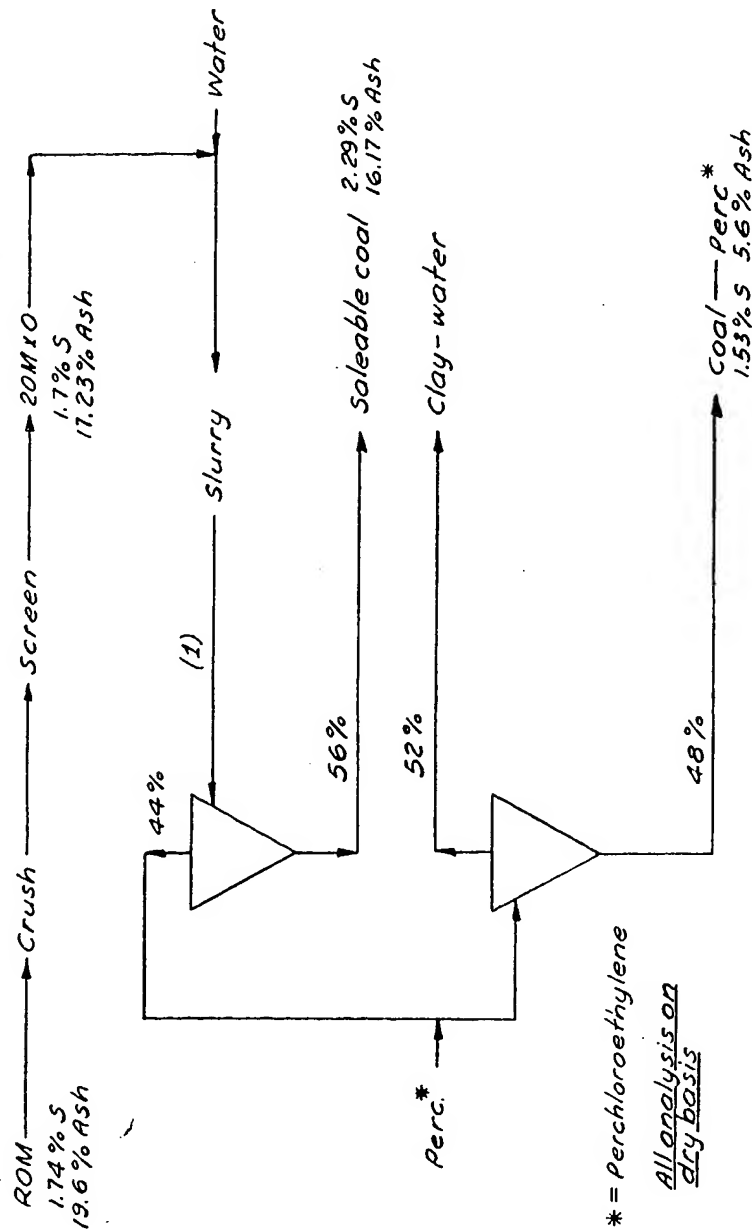


Fig. 2



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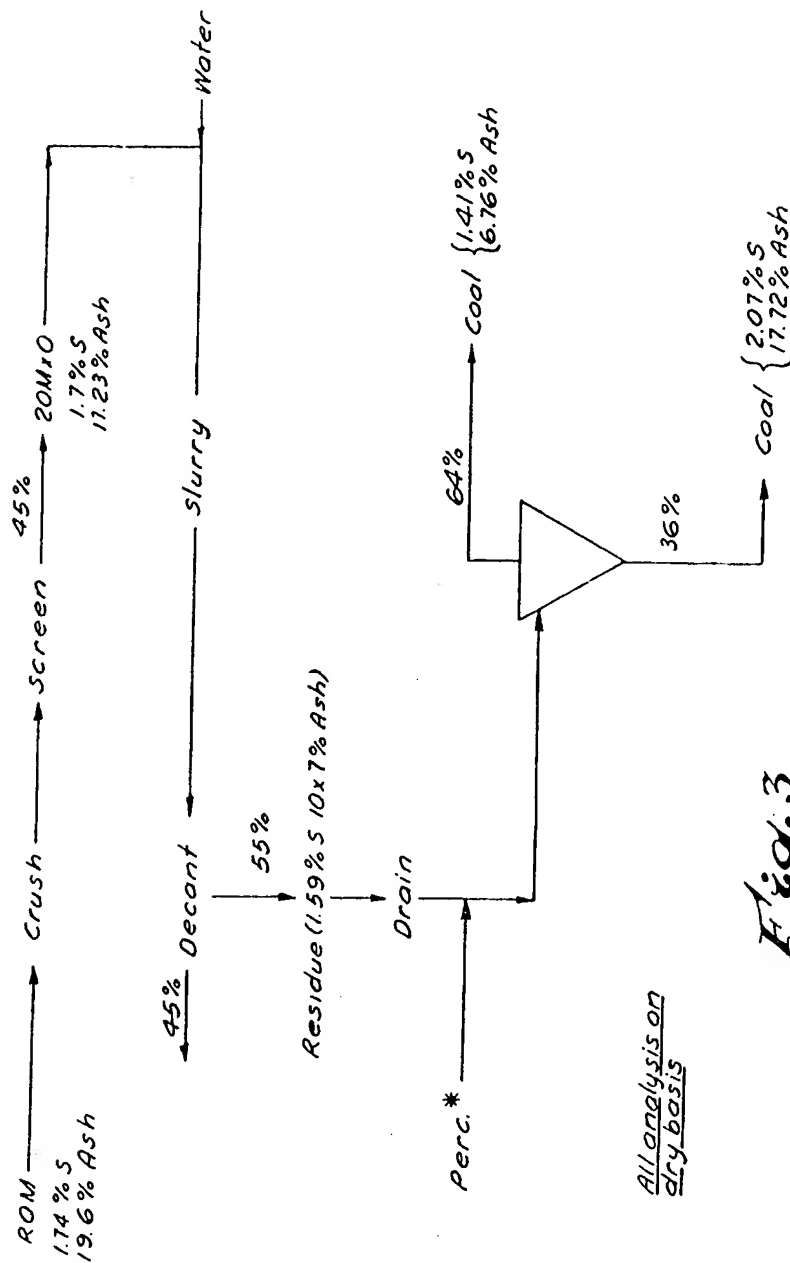


Fig. 3

All analysis on  
dry basis

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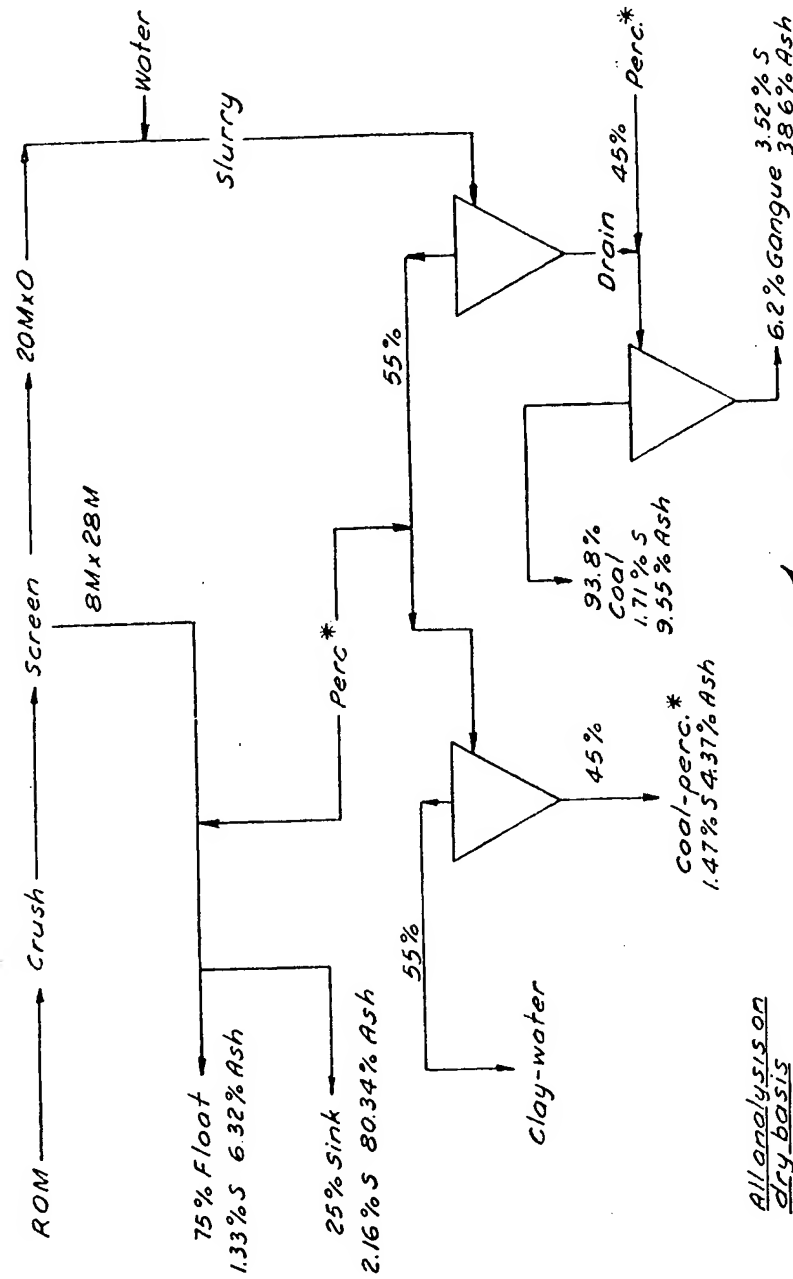


Fig. 4

All analysis on  
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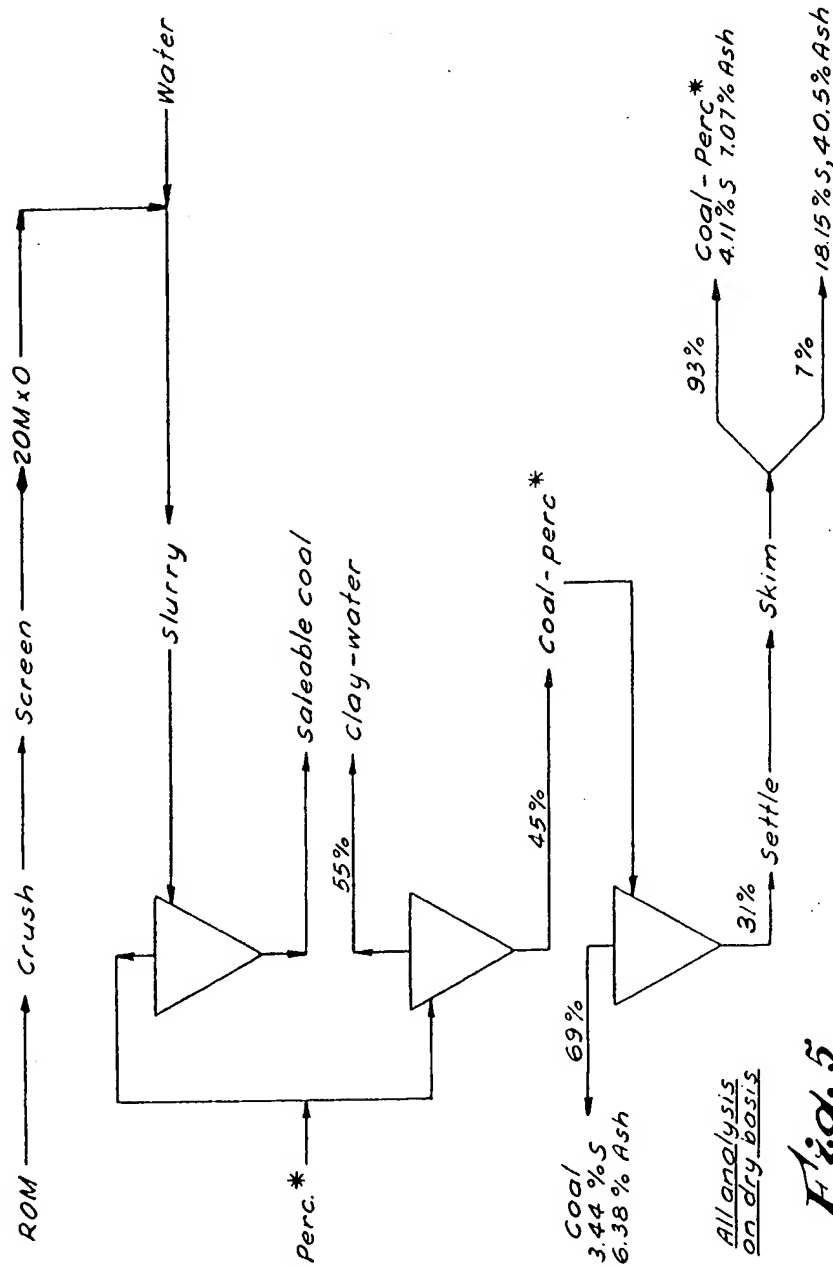


Fig. 5

